SALT-ADDED METHOD FOR BREAKING AZEOTROPE OF BINARY IPA-WATER SYSTEM: USING ASPEN PLUS

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I declare that this thesis entitled “Salt-added Method for Breaking Azeotrope of Binary IPA and Water System: Using Aspen Plus” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....

Name : .....

Date : .....

To the missing pieces of courage and hope.
May it soon find its way home.

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ABSTRACT

Distillation process is a method for separating various components of a liquid solution depending upon the distribution of these components between a vapour phase and a liquid phase. It is commonly used as a solvent recovery method, a technology in many areas of pharmaceutical and especially chemical industries. IPA is a rubbing alcohol used as cleaner and solvent in industries. It forms azeotrope with water that ordinary distillation can never separate both components directly. Mostly in industries, azeotropy and highly nonideal behavior during distillation complicates the recovery of solvents and the not recovered solvents usually end up as toxic waste. Apart from that, the interest of this project is to study the azeotrope breaking of binary IPA-water system with salt-added method to recover purity of IPA by using batch distillation in the Aspen Plus environment. Then, the concentration of salt added to break the azeotrope of IPA-water system in batch distillation process is investigated. After coming up with a simulation solution based on the optimum condition of chosen parameters, the result show that the azeotrope breaking of binary IPA-Water system with salt added method is not successful by using batch distillation via simulation of Aspen Plus. The azeotropic point of the binary IPA-Water system has only shifted but failed to break. Thus, it is recommended to do an experimental of the batch distillation in order to understand more of the salt-added method in breaking the azeotope system and then to implement the same method in simulation to achieve the objective.

ABSTRAK

Process penyulingan adalah satu cara untuk mengasingkan komponen-komponen larutan cecair yang pelbagai berdasarkan pengagihan komponen ini di antara fasa gas dan fasa cecair. Ia secara umumnya diguna sebagai cara untuk mandapatkan larutan yang tertentu, satu teknologi dalam pelbagai bidang farmasi dan lebih-lebih lagi dalam bidang industri kimia. IPA ialah sejenis alkohol yang digunakan sebagai pembersih dan pelarut dalam pelbagai industri. Ia membentuk azeotrope dengan air yang mana penyulingan biasa tidak mampu mengasingkan kedua-dua komponen secara terus. Kebanyakan di dalam industri, azeotrope dan ciri-ciri yang tidak ideal semasa penyulingan menyukarkan penghasilan larutan tersebut dan kebanyakannya penghasilkan bahan buangan bertoksik. Tujuan projek ini ialah untuk mengkaji pemecahan azeotrope di dalam sistem IPA-air dengan cara menambahkan garam untuk mengembalikan ketulenan IPA dengan menggunakan penyulingan berkelompok secara simulasi menggunakan Aspen Plus. Kemudian, untuk mengkaji pengkhususan terhadap penambahan garam untuk memecahkan azeotrope dalam sistem IPA-air dalam proses penyulingan berkelompok. Selepas menjalankan simulasi penghasilan yang berdasarkan parameter yang dipilih berdasarkan keadaannya pada tahap optimum, kajian dalam memecahkan azeotrope bagi sistem IPA-air dengan cara penambahan garam tidak berjaya dengan menggunakan penyulingan berkelompok secara simulasi dalam Aspen Plus. Titik azeotropik pada sistem berganda IPA-air hanya berubah dan gagal di pisahkan. Oleh itu, dicadangkan bahawa satu kajian melalui eksperimen penyulingan berkelompok dijalankan untuk meningkatkan pemahaman terhadap pemecahan sistem azeotrope dengan penambahan garam. Kajian yg sama juga dijalankan dengan menggunakan simulasi Aspen Plus untuk mencapai objektif projek.

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

1.1 Project Background

Distillation process is a method for separating the various components of a liquid solution depending upon the distribution of these components between a vapour phase and a liquid phase (C.J.Geankoplis, 2003). In this project, we focus more on the usage of Batch Distillation. It is commonly used as a solvent recovery method, a technology in many areas of pharmaceutical and especially chemical industries (I.R-Donis, E.P-Fondevila, V.Gerbaung, X.Joulia, 2001).

In the world of Chemical Engineering, solvent recovery is important to reduce the number of hazardous waste and pollutions. In the industries, IPA (Isopropyl Alcohol) is known as rubbing alcohol used as a cleaner and solvent. It is miscible with water, thus forming azeotrope with water at certain temperature. An azeotrope cannot be separated by ordinary distillation since no enrichment of the vapour phase occurs at this point. Therefore, in most cases, azeotropic mixtures require special methods to facilitate their separation such as a mass separating agent like a membrane-material for pervaporation or an entrainer for extractive distillation. Extractive and heteroazeotropic distillation are the most common methods to break this azeotrope behaviour. In this project, the salt added method is used to break the azeotrope of IPA-Water system. Sodium Chloride (NaCl) is used in this process as the entrainer.

Aspen Plus is used to conduct the simulation of process involves in an existing plant. It is a tool that can help engineers to predict the behaviour of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. With reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, they can simulate actual plant behaviour.

1.2 Project Problem Statement

Solvent recovery is important in a fine- and specialty chemical industries. The recovery and reuse of organic solvent is generally practiced because of the increasing of solvent cost and potential solvent shortages. IPA is known as rubbing alcohol used as cleaner and solvent in industries. It forms azeotrope with water at 80.37^{o}C that ordinary distillation can never separate both components directly. Mostly in industries, azeotropy during distillation complicates the recovery of solvents and the not recovered solvents usually end up as toxic waste. Other than that, disposal of waste is often results in violation of air-, water-, or land-pollution regulation (Eva-Katrine Hilmen, 2000).

The problem in this situation is the difficulty of the separation due to the azeotropic state of IPA-Water system and the way to comprehend the process without ever going to put up a bench scale or pilot plant. Even by improving a readily built plant, it will costs time and money and it is one of the challenges faced by Process Engineers these days. Experience alone is not always sufficient to answer the questions that continually arise and ‘trial and error’ efforts to provide meaningful insight is costly and potentially dangerous. Thus, this requires cost-effective tools that help identify and ‘correct’ the anticipated problems before they occur.

1.3 Project Objectives

1. To study the azeotrope breaking of binary IPA-water system with salt-added method to recover purity of IPA by using batch distillation in the Aspen Plus environment.
2. To investigate the concentration of salt added to break the azeotrope of IPA-water system in batch distillation process.

1.4 Project Scopes

In order to achieve the objective of the project, some boundary or scope need to be specified. This project covers the breaking of azeotrope of binary IPA-Water system, salt added method, batch distillation and Aspen Plus.

Firstly, the salt added used in this project is sodium chloride (NaCl). It is chosen for it's highly availability and also it is the most common salt used in the industries, for example in manufacturing of pulp, textile and detergent products. The concentration of sodium chlorides use in this project will vary to get the optimum concentration.

Secondly is to run several simulations using Aspen Plus to get optimum results. So, certain parameters will take place in order to achieve the objective. The parameters consist of:

- concentration of salt added
- time constraints
- reflux ratio

CHAPTER 2

LITERATURE REVIEW

2.1 Batch Distillation

Separation process plays a big role in chemical engineering. In general, separation of homogeneous liquid mixtures requires the creation or addition of another phase within the system. The most common method is repeated vaporization and condensation – distillation (Eva-Katrine Hilmen, 2000). Distillation process is a method for separating the various components of a liquid solution depends upon the distribution of these components between a vapour phase and a liquid phase (C.J.Geankoplis, 2003). Alternatives to distillation are adsorption, membrane separation, crystallization, liquid-liquid extraction, chromatography and others (Smith, 1995).

In this project, the focus is on the area of batch distillation. Batch distillation is one of the solvent recovery methods, a technology in many areas of pharmaceutical and especially chemical industries (I.R-Donis et. al, 2001) but why batch distillation? Batch distillation is less energy efficient than continuous distillation and it offers possibility of separating multi-component mixtures into high purity products using single columns. So, it is less expensive compared to continuous distillations that required (n-1) columns. It is flexible and robust to variation in feed composition and specification. It is important for production of seasonal or low capacity chemicals. Batch distillation also can be used for liquids with contaminants such as solids, tars and resins. (Rousseau, 1987)

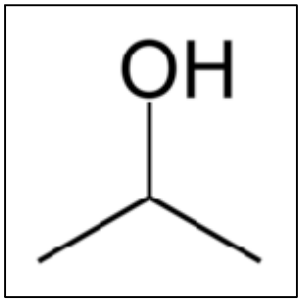
"Designing equipment for such [azeotropic] separations is a real challenge to the distillation engineer. Often, sufficient data are not available for complete calculation so that the process must be developed in the laboratory, or, at least, assumptions checked. Combinations of continuous and batch distillations, decanting, multistage extraction, and chemical treatment may often be combined in a successful process."
Drew as quoted by Schweitzer (1997)

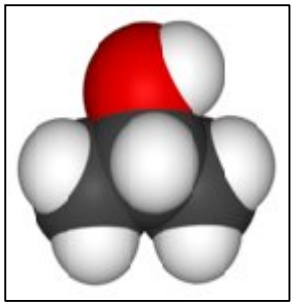
From the above statement from Schweitzer (1997), azeotrope behaviour has put many engineers up for challenges in designing distillation. To date, there has been many kind of distillation methods that fit for azeotropic separations such as the extractive distillation, combination of column and decanting distillation and also reactive distillation.

2.2 IPA-Water System

2.2.1 IPA

IPA is a short form for Isopropyl Alcohol. Known as rubbing alcohol, Isopropyl alcohol or Isopropanol is a secondary alcohol with chemical formula C_3H_8O. It is colourless and has a strong odour that resembles ethanol. IPA has high flammability with a very wide combustible range. Its vapour is heavier than air and it can explode through deflagration. It is commonly used as a cleaner agent and solvent in industry such as a cleaning agent for electronic devices (CDs, DVDs, cell phones, etc). It is also used in "dry-gas" fuel additives. If poisoned, it can cause symptoms such as dizziness, nausea and fatal whereas a long term on skin can cause defatting. IPA is totally miscible in water. For example as the fuel additives, it completely mixed with water in the supply fuel lines that keep away insoluble water especially during freezing season. IPA forms azeotrope with water at 87.4 mass% alcohols at temperature 80.37^{o}C. Since in this project we focus on breaking the azeotrope, it is known that IPA can be separated from aqueous solutions for example water by adding salt (NaCl, Na_2SO_4 or inorganic salts)





a) IPA – Skeletal view

b) IPA – 3D view

Figure 2.1 : IPA skeletal view and 3D view

Table 2.1 : Physical & Chemical Properties of IPA

Isopropyl alcohol	
General	
Systematic name	Propan-2-ol
Other names	2-propanol, isopropanol, Isopropyl alcohol
Molecular formula	C_3H_8O
Molar mass	60.10 g/mol
Appearance	Colourless liquid
Properties	
Density and phase	0.785 g/cm^3, liquid
Solubility in water	Fully miscible
Solubility in brine	Slightly soluble
In ethanol, ether In acetone, toluene	Fully miscible Soluble
Melting point	-89 °C (185 K)
Boiling point	82.3 °C (355 K)
Acidity (pK_a)	16.5 for H on hydroxyl
Viscosity	2.86 cP at 15 °C 1.77 cP at 30 °C
Dipole moment	1.66 D (gas)

2.2.2 Water

Water is mainly the most important substance in the world. It is a chemical substance consists of 2 of hydrogen atom and one oxygen atom. It is tasteless, odourless liquid at ambient temperature and pressure. Water appeared to be colourless or more to a very light blue hue. It is also known as the universal solvent.

Figure 2.2 : Water skeletal view and 3D view

Table 2.2 : Physical & Chemical Properties of Water

Water	
General	
Systematic name	Water
Other names	Aqua, dehydrogen monoxide, hydrogen hydroxide
Chemical formula	H_2O
Molar mass	18.0153 g/mol
Properties	
Density and phase	0.998 g/cm³ (liquid at 20 °C) 0.92 g/cm³ (solid)
Melting point	0 °C (273.15 K) (32 °F)
Boiling point	100 °C (373.15 K) (212 °F)
Specific heat capacity	4.184 J/(g•K) (liquid at 20 °C)

2.2.3 IPA-Water Binary System

At atmospheric condition, a binary mixture of 2-propanol (isopropyl alcohol, IPA)–water forms a homogeneous minimum-boiling azeotrope at 87.4–87.7 mass% and 80.3–80.4 ◦C. Some investigations have reported that IPA–water azeotrope can also be broken with other azeotropic distillations to form heterogeneous azeotropic systems by adding one of the following entrainers: isopropyl ether, benzene, methyl ethyl ketone, and isopropyl acetate. Sometimes, ethyl ether is used as entrainer at pressures substantially above atmospheric (R.D. Kirk, D.F. Othmer, Encyclopedia of Chemical Technology, vol. 16, second ed., John Wiley and Sons Inc., NY, 1968)

2.3 Vapour-Liquid Phase Equilibrium, Nonideality and Azeotropy

At low to moderate pressures and temperatures away from the critical point, the vapour-liquid phase equilibrium for a multicomponent mixture may be expressed as:

$$y_i\ P \quad = \quad x_i\ \gamma_i(T, \boldsymbol{x})\ P_i^{sat}(T), \qquad i = 1, 2, ..., n \tag{2.1}$$

where yi and xi are the vapor and liquid compositions of component i, respectively, P and T are the system pressure and temperature, i is the activity coefficient of component i in the liquid phase, and Psat i is the saturated vapor pressure of component i. The activity coefficient i is a measure of the nonideality of a mixture and changes both with temperature and composition. When i = 1, the mixture is said to be ideal and Equation (8.2) simplifies to Raoult's law:

$$y_i\ P = x_i\ P_i^{sat}(T), \qquad i = 1, 2, ..., n \tag{2.2}$$

Nonideal mixtures exhibit positive (i > 1) or negative (i < 1) deviations from Raoult's law. If these deviations become so large that the vapor pressure exhibits an extremal point at constant temperature, or, equivalently, an extremal point in the boiling temperature at constant pressure, the mixture is *azeotropic*. At azeotropic points, the liquid phase and its equilibrium vapor phase have the same composition x = y, and the condensation and boiling temperature curves are tangential with zero slope (see Figure 2.1a).

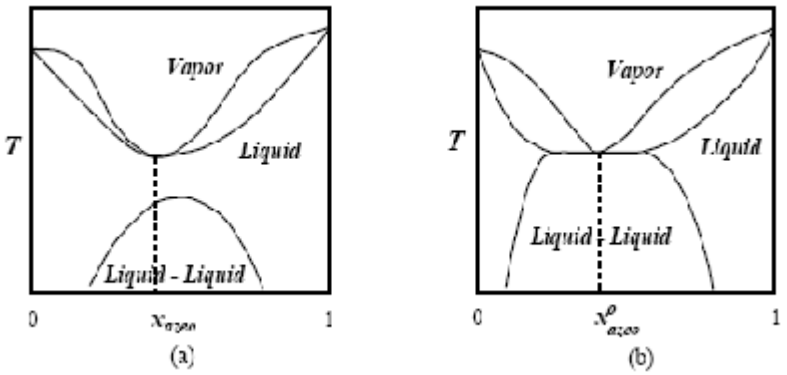


Figure 2.3 : Azeotropes may be homogeneous or heterogenous: (a) minimum-boiling homoazeotrope (b) heteroazeotrope.

If the positive deviations are sufficiently large (i > 4, typically), phase splitting may occur and form a heteroazeotrope where the vapor phase is in equilibrium with two liquid phases (see Figure 2.1b). In the heteroazeotropic point the overall liquid composition $x_{o\ azeo}$ is equal to the vapor composition, and the vapor and liquid temperature surfaces are tangential with zero slopes, but the three coexisting phases have distinct compositions. In ternary and multicomponent systems *saddle* azeotropes may occur, which Swietoslawski (1963) call *positive-negative* azeotropes.

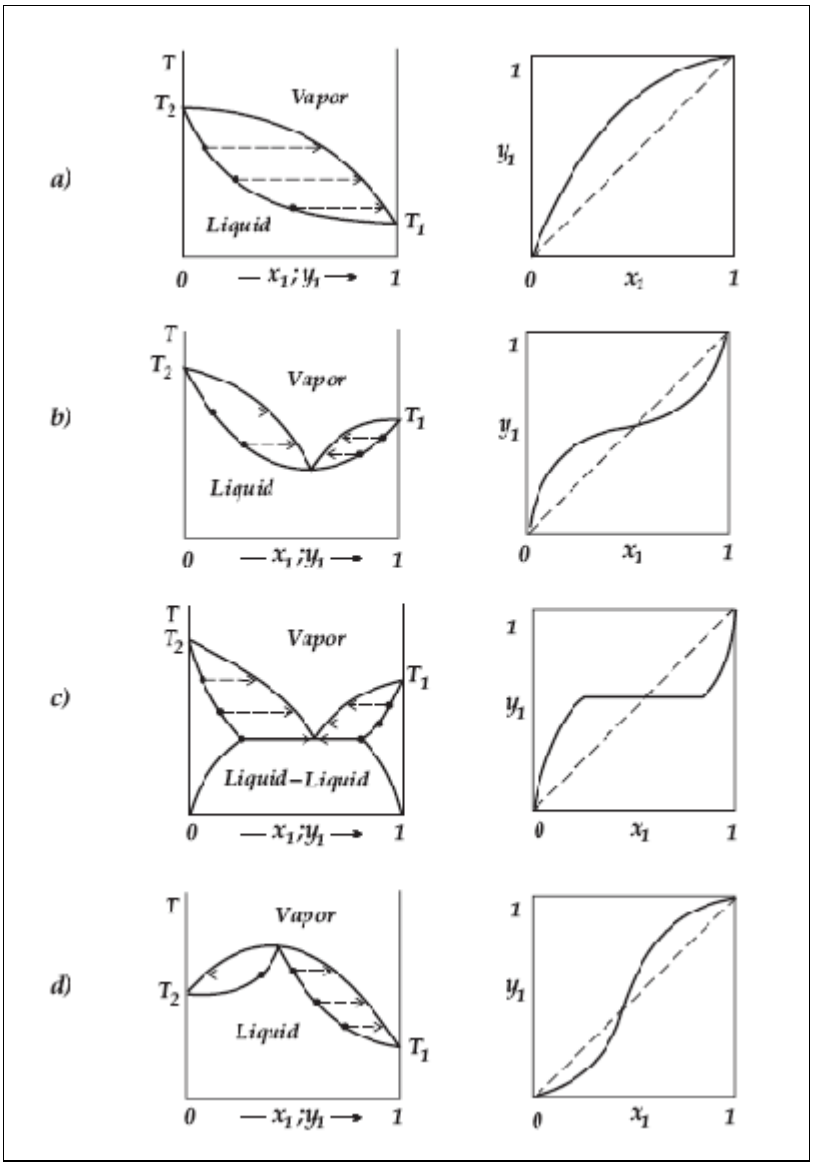


Figure 2.4: Graphical representations of the VLE for the most common types of binary mixtures at constant pressure: a) zeotropic; b) minimum-boiling homoazeotrope; c) minimum-boiling heteroazeotrope;d) maximum-boiling azeotrope. Left: boiling temperature T_{bp} and condensation temperature T_{dp} and the equilibrium mapping vectors in T = x; y space. Right: x - y relationship (equilibrium line)

2.3.1 Binary Vapor-Liquid Equilibrium Data

This is an example of binary vapor-liquid equilibrium data of Isopropanol and water within the pressure of 760mmHg.

Table 2.3 : Binary Vapor-Liquid Equilibrium Data

Vapor-liquid Equilibrium for Isopropanol/Water[2] *P* = 760 mm Hg		
BP Temp. °C	**% by mole isopropanol**	
	liquid	**Vapor**
82.2	100.00	100.00
81.48	95.35	93.25
80.70	87.25	83.40
80.37	80.90	77.45
80.23	76.50	73.70
80.11	69.55	69.15
80.16	66.05	67.15
80.15	64.60	66.45
80.31	55.90	62.55
80.38	51.45	60.75
80.67	44.60	59.20
80.90	38.35	57.00
81.28	29.80	55.10
81.29	29.75	55.40
81.23	28.35	55.30
81.62	24.50	53.90
81.75	19.35	53.20
81.58	18.95	53.75
81.99	16.65	52.15
82.32	12.15	51.20
82.70	10.00	50.15
84.57	5.70	45.65
88.05	3.65	36.55
93.40	1.60	21.15
95.17	1.15	16.30
100.0	0.00	0.00

2.3.2 Vapor-Liquid Equilibrium Graph

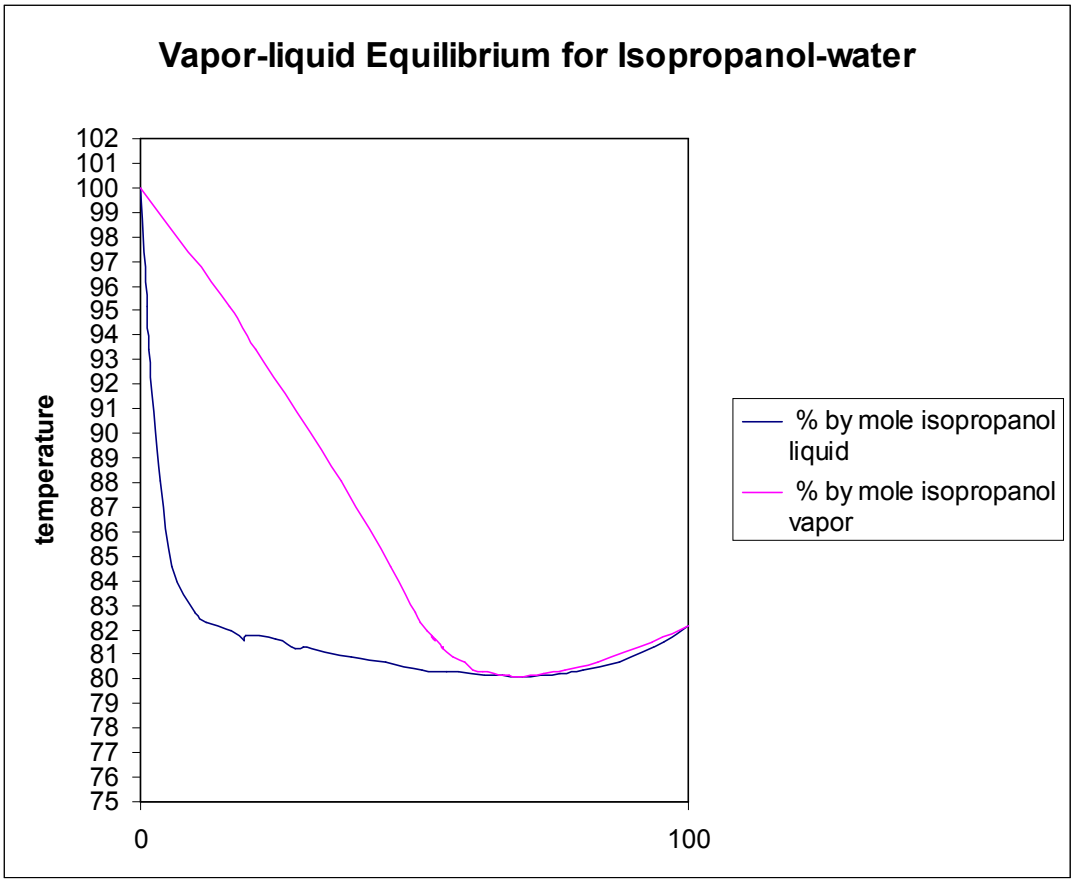


Figure 2.5 : Vapor-Liquid Equilibrium Graph

The graph above is plotted using Microsoft Excel. The graph shows that the IPA and Water have the minimum azeotrope boiling point.

2.4 Azeotrope and Entrainer

"An understanding of azeotropes is desirable for two reasons. First, they often occur in distillation and make a given separation impossible by ordinary distillation. Secondly, they may be utilized to separate mixtures not ordinarily separable by straight distillation." Ewell *et al.* (1944)

The term azeotrope means "nonboiling by any means" (Greek: a - non, zeo - boil, tropos - way/mean), and denotes a mixture of two or more components where the equilibrium vapor and liquid compositions are equal at a given pressure and temperature (Eva-Katrine Hilmen,2000). It was Wade and Merriman who had first introduce the term azeotrope in 1911 to designate mixtures that have a minimum or maximum boiling point at constant pressure (Doherty & Malone, 2001) or, equivalently, in the vapour pressure under isothermal conditions (Swietoslawski, 1963; Malesinkski, 1965). They define the azeotropy state as a stationary point in the equilibrium T-x,y or P-x,y. The mixture whose composition corresponds to an extremal point is called an azeotrope. If at the equilibrium temperature the liquid mixture is homogeneous, the azeotrope is a homoazeotrope. If the vapor phase coexists with two liquid phases, it is a heteroazeotrope. Systems which do not form azeotropes are called zeotropic (Swietoslawski, 1963).

The formation of azeotrope is due to the differences in the intermolecular forces of attraction among the mixture components. There are 3 groups that particularly deviate from the ideality that simply explains the binary mixtures (Eva-Katrine Hilmen,2000). They are :

1. *Positive deviation from Raoult's law:* The components "dislike" each other. The attraction between identical molecules (A-A and B-B) is stronger than between different molecules (A-B). This may cause the formation of a minimum-boiling azeotrope and heterogeneity.

2. *Negative deviation from Raoult's law:* The components "like" each other. The attraction between different molecules (A-B) is the strongest. This may cause the formation of a maximum-boiling azeotrope.

3. *Ideal mixture obeys Raoult's law:* The components have similar physiochemical properties. The intermolecular forces between identical and different molecules (A-A, B-B and A-B) are equal.

The tendency a mixture to form an azeotrope depends on 2 factors (Horsely, 1973; King, 1980):

1. the differences in the pure component boiling point
2. the degree of nonideality

Due to azeotrope and resulting phase behaviour, there are profound effects on the feasibility and technology for distillation-based operation.

2.4.1 Entrainer-addition Distillation Methods

A Physiochemical change of the VLE behaviour of an azeotropic mixture by the addition of an extraneous liquid component offers a number of possibilities. We name the mixture to be separated as the *original mixture*, and the added component that facilitates the separation the *entrainer*. For the purpose of ease of visualization, we limit our considerations to binary homoazeotropic original mixtures and one-component entrainers. The same separation techniques apply to multicomponent mixtures where the key components form characteristic mixtures falling into the categories discussed, and the entrainer may be a mixture of components.

We distinguish between three different conventional entrainer-addition based distillation methods depending on the properties and role of the entrainer and the organization (scheme) of the process (Eva-Katrine Hilmen,2000):

1. ***Homogeneous azeotropic distillation*** (ordinary distillation of homoazeotropic mixtures): The entrainer is completely miscible with the components of the original mixture. It may form homoazeotropes with the original mixture components. The distillation is carried out in a conventional single-feed column.

2. ***Heteroazeotropic distillation*** (decanter-distillation hybrids that involve heteroazeotropes): The entrainer forms a heteroazeotrope with at least one of the original mixture components. The distillation is carried out in a combined column and decanter system.

3. ***Extractive distillation***: The entrainer has a boiling-point that is substantially higher than the original mixture components and is selective to one of the components. The distillation is carried out in a two-feed column where the entrainer is introduced above the original mixture feed point. The main part of the entrainer is removed as bottom product.

4. **Reactive distillation***:* The entrainer reacts preferentially and reversibly with one of the original mixture components. The reaction product is distilled out from the non-reacting component and the reaction is reversed to recover the initial component. The distillation and reaction is usually carried out in one column (catalytic distillation).

5. **Chemical drying (chemical action and distillation)***:* The volatility of one of the original mixture components is reduced by chemical means. An example is dehydration by hydrate formation. Solid sodium hydroxide may be used as an entrainer to remove water from tetra hydro furan (THF). The entrainer and water forms a 35-50 % sodium hydroxide solution containing very little THF (Schweitzer, 1997).

6. **Distillation in the presence of salts:** The entrainer (salt) dissociates in the mixture and alters the relative volatilities sufficiently so that the separation becomes possible. A salt added to an azeotropic liquid mixture will reduce the vapor pressure of the component in which it is more soluble. Thus extractive distillation can be applied using a salt solution as the entrainer. An example is the dehydration of ethanol using potassium acetate solution (Furter, 1968).

2.4.2 Sodium Chloride (NaCl) as Entrainer

2.4.2.1 Sodium Chloride

Sodium chloride is commonly known as the common salt, table salt or halite. It is a chemical compound with formula NaCl. It is responsible of the salinity of the ocean and also the extracellular fluid of multicellular organism. Sodium chloride can be produced by a) the evaporation of sea water b) brine such as brine wells and salt lakes and c) mining rock salt (halite). Approximately 0.3933 gram of sodium and 0.6067 gram of chlorine is found in 1 gram of NaCl. The usage of salt varies from the manufacturing of pup & paper to setting dyes in textiles & fabrics till the products of soaps & detergents. It is commonly used as flavour enhances, producing chlorine in synthetic uses (PVC & pesticides) and also the road salts (De-icing salt).